The Hydrophobic Character of Semisoluble Salt Minerals with Oleate as Collector

by

J.D. Miller and M. Misra
University of Utah
U.S.A.

Synopsis

The effects of temperature, oxygen partial pressure, and solution chemistry can have a significant effect on the hydrophobic character of semisoluble salt minerals with adsorbed oleate. Measurements of bubble-attachment time and contact angle reveal the sensitivity of these hydrophobic surfaces to changes in such variables. These results suggest that the interaction of the unsaturated oleyl chains is important. This interaction seems to be a rather complex phenomenon and may involve the oxidation of the double bond and subsequent cross-linking between adjacent oleyl chains.

INTRODUCTION

One of the most important collectors in the flotation of semisoluble salt minerals is oleic acid. Although considerable research has been reported on the solution chemistry, the oleate adsorption reaction (chemisorption/chemical reaction), and the flotation response, little attention has been given to the hydrophobic character of these systems. After a review of these former topics, the hydrophobic character of semisoluble salt minerals with adsorbed oleate will be discussed in terms of measurements of the bubble-attachment time and the contact angle. The oleate adsorption and subsequent flotation of nonsulphide minerals depends on the extent of hydrolysis of the mineral surfaces and the oleate solution chemistry.

OLEATE SOLUTION CHEMISTRY

The nature of the oleate species existing in solution depends on the extent of hydrolysis, which is highly pH dependent[1]. In addition, these aqueous species have a tendency to undergo associative interactions among themselves and with other species by virtue of hydrophobic bonding between the hydrocarbon chains. This phenomenon gives rise to the formation of molecular aggregates even below the critical micelle concentration[2]. The surface activity of these aggregates may be different from that of the individual species from which they are formed. Therefore, associative interactions as well as the nature of the individual species are expected to affect adsorption, flotation, and the hydrophobic character of mineral surfaces significantly.

Hydrolysis

The study of oleate solutions has provided evidence that indicates the existence of oleate ion ($RCOO^-$), oleate dimer ($(RCOO)_2^{2-}$)[3], free oleic acid (RCOOH), and another ionomolecular species ($RCOOH \cdot RCOO^-$), known as the acid-soap[4].

Several equilibrium constants have been considered for the hydrolysis reaction of oleic acid[4-6]. Somasundaran *et al.*[1] computed a species-distribution diagram for an oleate concentration of $3{,}0 \times 10^{-5}$ M, as shown in Figure 1.

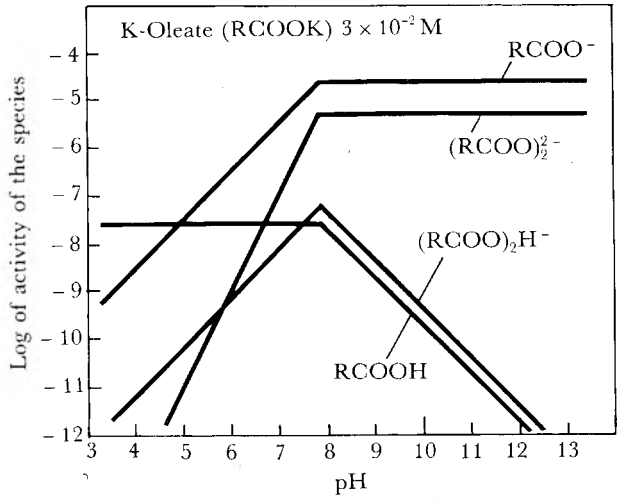


Figure 1. Species distribution diagram for an aqueous oleate solution[1]

It is seen from the figure that

- the maximum activity of the ionomolecular species ($RCOOH \cdot RCOO^-$) occurs at a pH value of 7,8 for a total oleate concentration of $3,0 \times 10^{-5}$ M,
- the activities of the ionic oleate ($RCOO^-$) and its dimer ($(RCOO)_2^{2-}$) increase as pH is increased up to a value of 7,8 and then remain constant at higher pH values, and
- neutral oleic acid (RCOOH) starts to precipitate from the aqueous solution at pH values below 7,8.

So the activities of all species inhibit an abrupt change at a pH value of 7,8.

A similar diagram was constructed by Jung[5] from Mukerjee's original model[6] and a total oleate concentration of 10^{-2} M. This analysis similarly shows abrupt changes near a pH value of 8 as well as at a value of 11 for all species. Furthermore, the concentrations of $(RCOO)^-$ and $(RCOO)_2^{2-}$ keep increasing even beyond a pH value of 8 and level off only after a value of 11. In both cases, the concentration of the ionomolecular species ($RCOOH \cdot RCOO^-$) is less than that of the ionic oleate and its dimer by orders of magnitude at any specific value of pH.

Associative interactions

Zimmels and Lin[2] have studied the stepwise association of soaps in aqueous solutions and have defined the critical micelle concentration (C.M.C.) as a narrow range of concentrations above which additional surfactant molecules are transformed mainly into associated (micelle) forms. Conventionally, there is only one critical micelle concentration, which for sodium oleate occurs at $2,1 \times 10^{-3}$ M. However, premicellar association has also been established. As can be seen from Figure 2, the curve has three sharp changes in slope at $1,7 \times 10^{-5}$ M, $4,6 \times 10^{-4}$ M, and $2,1 \times 10^{-3}$ M, which have been attributed to three associative forms, the last one being the conventional C.M.C. Cook[7] has quantitatively established the role of the premicellar associations and explained the hydrolysis behaviour, as have Stainsby and Alexander[8].

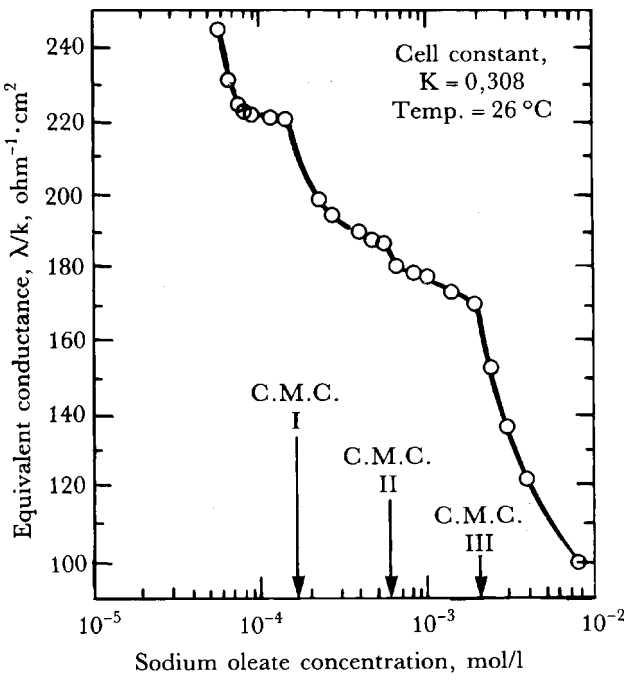


Figure 2. Equivalent conductance of sodium oleate solutions as a function of oleate concentration[2]

As long as the soap is the only monomer formed at high dilutions, the hydrolysis is governed by the simple mass-action equations, but, once the association becomes significant, these equations[4] are no longer sufficient[9]. As a result, it is expected that other factors must be considered under such conditions in order to explain optimum flotation at the maximum acid-soap concentration, as has been suggested by some researchers[1,4]. Association has a great influence on flotation and adsorption, but this aspect was not given proper attention in the past. Zimmels *et al.*[10] in 1975 developed a semiquantitative relation between the stepwise bulk association and its effect on different interfacial properties, such as adsorption density.

Summary

There is a difference of opinion expressed in the literature with regard to the most important oleate species for adsorption and flotation. Somasundaran *et al.*[1] as well as Jung[5] consider the ionomolecular species ($RCOOH \cdot RCOO^-$) as the most surface-active species, responsible for maximum flotation. On the other hand, Dixit *et al.*[11] consider the ionic oleate ($RCOO^-$) (and presumably dimer) as the active species. Perhaps such conjectures based on correlations with flotation response are not entirely appropriate and other evidences should be sought.

ADSORPTION PHENOMENA

Oleic acid forms stable, sparingly soluble salts with alkaline-earth and heavy-metal cations and, as a result, has good utility as a collector for semi-soluble salt minerals, many of which contain calcium: calcite, apatite, scheelite, and fluorite. The formation of the calcium oleate salt either from solution or at the mineral surface would be expected from solution-chemistry calculations.

Infrared spectroscopy has been used to establish the chemical nature of the oleate adsorption reaction[12,13]. The adsorption of oleate by semi-soluble salt minerals has been studied by several investigators. For example, the adsorption of oleate by fluorite was studied by French *et al.*[14]. Subsequently Peck[12] studied the adsorption of oleate by calcite and barite in addition to fluorite. The chemisorption of oleic acid and oleate was proposed for calcite, barite, and fluorite.

Other studies have been limited to adsorption density measurements. Somasundaran[15] suggested that oleate is coulombically adsorbed by calcite and apatite below the respective P.Z.C.s. Infrared studies suggest a chemisorption or chemical reaction. In addition, the nature of oleate adsorption by fluorite has been studied by Bahr[16] and also by Calara[17].

Considerable research has been reported on the adsorption of oleate by fluorite, which will be examined as a case study.

Infrared spectroscopy

Although the formation of surface calcium oleate species has been found for a modest alkalinity, evidence has also been presented for physically adsorbed sodium oleate at higher pH values and oleic acid at lower pH values close to the pK_a of oleic acid[12]. The distribution of surface species is presented in Figure 3 as a function of pH. Other investigators claim that the surface species are not uniquely distinguished by the infrared spectra.

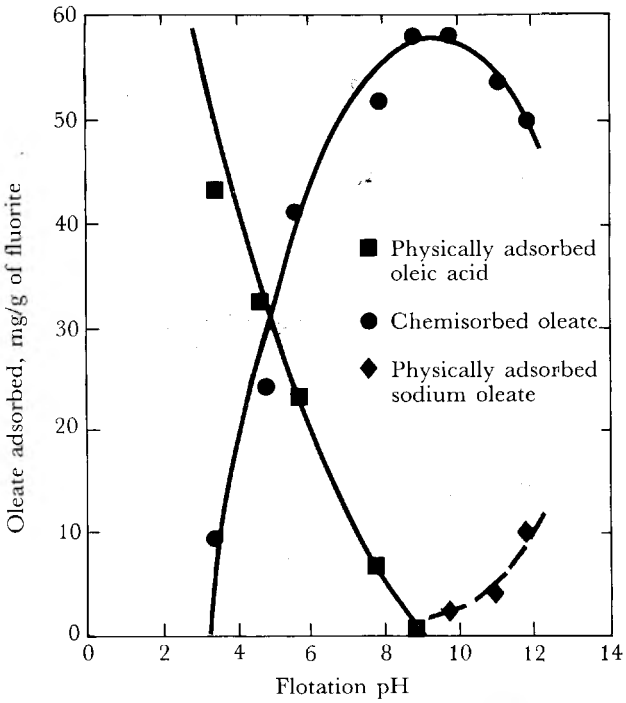


Figure 3. Distribution of adsorbed oleate species on the surface of fluorite as a function of pH[12]

Lovell *et al.*[13] obtained typical infrared surface spectra that confirm the results of French *et al.*[14] and Peck[12], but noted that the evidence for chemisorption is based more clearly on the observed irreversibility of adsorption and coverage at less than a monolayer. These investigators agree that the surface calcium oleate species is evidenced by a strong absorption band at 1562 cm^{-1} with a shoulder at 1613 cm^{-1} and suggest that these bands are essentially identical to sodium oleate salts because of the nature of surface bonding. Thus it is generally agreed that, besides calcium oleate being chemically bonded at the surface, oleic acid and sodium oleate could physically adsorb on fluorite and other semi-soluble minerals. The fraction, and actual amount, of oleate that is weakly bonded to the surface depends on pH of the system, as shown in Figure 3.

Measurements of the adsorption density

A Langmuir adsorption isotherm has been reported by Bahr[16] to describe the chemisorption or chemical reaction of oleate at the fluorite surface for equilibrium concentrations of up to 10^{-4} M sodium oleate. At oleate concentrations exceeding 10^{-4} M, Bahr[16] found an unexpected rise beyond monolayer coverage for the adsorption of oleate on the CaF_2 surface, measuring three effective monolayers at a concentration of 2×10^{-4} M.

Lovell *et al.*[13] also found adsorption beyond a monolayer at $5{,}3 \times 10^{-5}$ M oleate (as calculated from their reported data), which they attributed to physically adsorbed sodium oleate, although they could not ascertain this from the infrared spectra of the mineral. A rinse of the surface with boiling water reduced the adsorption density to a monolayer. Whether the excess oleate was in the form of sodium oleate or precipitated colloidal calcium oleate that would also wash away from the surface is an unresolved issue.

In this regard, an interesting finding by Bahr[16] was that, for oleate concentrations of less than 10^{-4} M, where the Langmuir isotherm was followed, the order of addition (CaF_2 added to the sodium oleate solution or sodium oleate solution added to a suspension of CaF_2) was not important. At concentrations larger than 10^{-4} M oleate, the adsorption density of oleate levelled off at about 10×10^{-6} mol/m^2 or just over monolayer coverage when dry CaF_2 was added to an oleate solution. On the other hand, when the fluorite was equilibrated with the water first and the oleate stock solution was then added, the measured adsorption density exceeded three monolayers at an equilibrium solution concentration of 5×10^{-4} M oleate. Also, measurements for the calcium concentration in the supernatant solution revealed that, before the adsorption maxima were reached, the calcium concentration exceeded that expected from solubility calculations. These results are presented in Figure 4 and suggest that, under certain circumstances, calcium oleate may be precipitated in the aqueous phase as a non-filterable colloid and could be construed to be adsorbed layers on the fluorite surface. Such a hypothesis would explain the multilayer adsorption that is observed and the apparent violation of the solubility product of calcium oleate. The

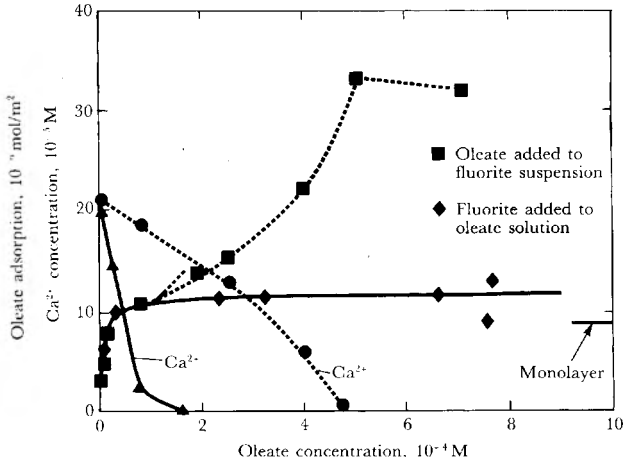


Figure 4. Adsorption density of oleate on fluorite and calcium ion concentration as a function of oleate concentration in solution[16]

validity of this supposition is easily demonstrated by adding to a saturated solution of CaF_2 enough oleate to make 50 mg/l at a pH value of 10. The solution will turn milky because of precipitated calcium oleate. An addition of dry-ground CaF_2 will clarify the solution.

FLOTATION BEHAVIOUR

Not unexpectedly, the flotation response of semi-soluble salt minerals with oleate as collector is similar since most of them contain alkaline-earth cations, particularly calcium. The Hallimond-tube flotation response for calcite, apatite, scheelite, and alunite is given as a function of pH (Figure 5)[18-20]. The flotation maxima in all cases are observed at slightly alkaline pH values. As mentioned previously, these results correlate with infrared and adsorption measurements.

Although flotation at modest alkalinities can be explained by the formation of surface calcium oleate species, the effect of other system variables, such as temperature and oxygen pressure, are not thoroughly understood.

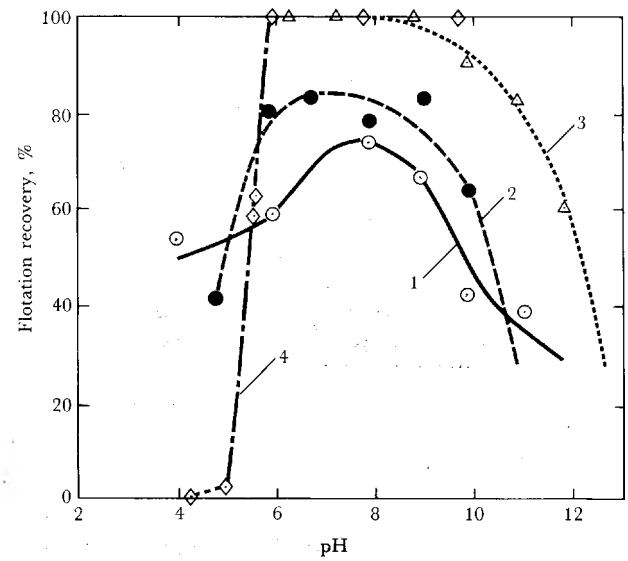


Figure 5. Oleate flotation of selected semisoluble minerals as a function of pH[18-20]. 1. Apatite, 10^{-5} M; 2, alunite, 10^{-4} M; 3. scheelite, 10^{-4} M; 4. calcite, 10^{-4} M

Temperature effect

Elevated temperatures appear to have a strong influence on the flotation of fluorite, but details of this effect at the molecular level are still undetermined. As early as 1925, Richards and Locke[21] reported this interesting dependence. Cook and Last[22] demonstrated that, as the temperature of a flotation pulp increased, the grade and recovery were enhanced considerably. The high-temperature concentrate was produced from a dry froth containing very little water and whose hydrophobic character did not change even with repeated cleanings. This was attributed to an activated adsorption process in which physically adsorbed collector proceeds through an activated state to a chemisorbed state. This explanation is not supported by infrared evidence, which clearly shows similar spectra for surface layers formed at both low and high temperature. Furthermore, it has been shown that increased temperature has little effect in fluorite flotation with saturated carboxylic acids—stearic and palmitic acids—when compared with the temperature dependence of fluorite flotation with oleic and linoleic acids.

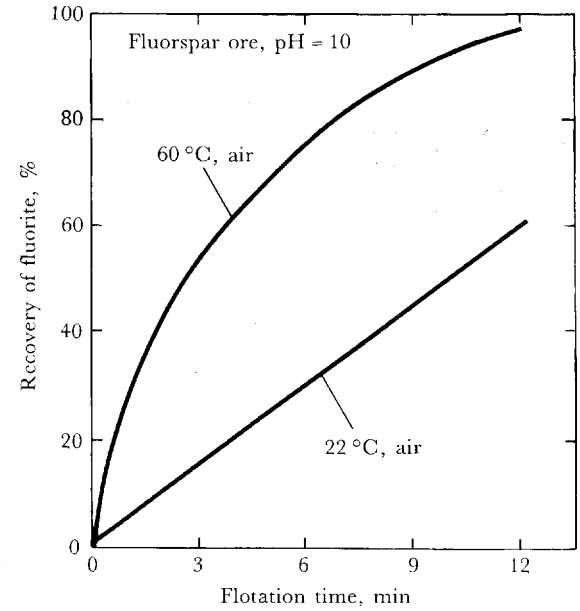


Figure 6. The effect of temperature on the flotation recovery of fluorite from a complex fluorspar ore

Recently in our laboratory, the dramatic effect of temperature on the flotation of fluorite from fluorspar was demonstrated, as shown in Figure 6. It can be seen that, for a high temperature, during the first five minutes from 60 to 80 per cent of the fluorite can be recovered, at a higher grade than that achieved under ambient conditions, where only 25 per cent of the fluorite can be recovered in five minutes.

Preliminary results obtained for the flotation of apatite in a Hallimond tube indicate a similar effect[20] (Figure 7). It can be noticed that apatite is

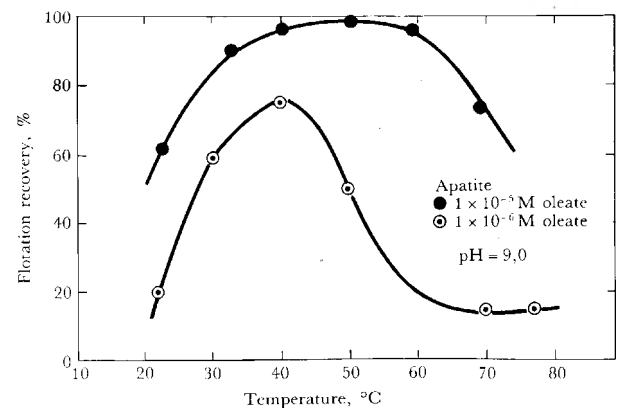


Figure 7. Flotation response of apatite as a function of temperature for two different oleate concentrations

very sensitive to temperature and exhibits a maximum that depends on the concentration of oleate.

Some researchers suggest that the temperature effect is due strictly to the state of aggregation of oleate in the aqueous phase[23]. When the oleate collector is dispersed properly, it is reported, excellent flotation can be achieved even at temperatures as low as 5 °C.

Nature of the hydrocarbon chain

It has been reported by Hukki[24] that the collecting power of fatty acids increases with increased unsaturation of the hydrocarbon chain. This may be due to an interaction of adjacent collector species at the surface through the double bond. The difference in flotation response does not appear to be a reflection of a change in the solubility products of the calcium/18C unsaturated carboxylates.

Oxygen effect

Another interesting effect is that the flotation of fluorite with oleic acid is enhanced when oxygen is used for flotation[25]. In this work, the effect of oxygen was stated to be a reversible effect, related to surface hydration phenomena. The flotation of calcite, phosphorite, and fluorite with oleic acid was reported to be enhanced when oxygen was used as the dispersing gas.

In our laboratory, experimental results from the bench-scale flotation of fluorite from a fluorspar ore have demonstrated this oxygen effect. The flotation rates for the recovery of fluorite from a fluorspar ore for experiments with an oxygen-saturated solution (oxygen >20 p.p.m.) are contrasted with the ambient flotation rate in Figure 8. The effect of oxygen on the flotation rate is evident. During the first five minutes, over 60 per cent of the fluorite can be recovered, under accelerated conditions, at a higher grade than that achieved under ambient conditions, where only 25 per cent of the fluorite can be recovered in five minutes.

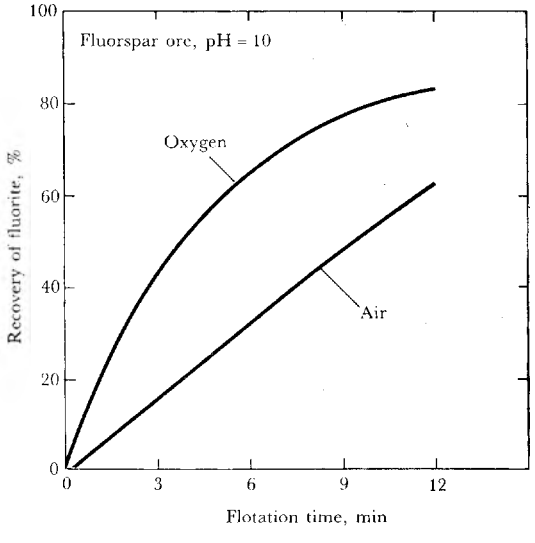


Figure 8. The effect of oxygen on the flotation recovery of fluorite from a complex fluorspar ore

A similar beneficial effect of oxygen was also observed for the flotation of apatite. After five minutes of conditioning with oxygen (oxygen >20 p.p.m.), the recovery of apatite increased from 60 to 78 per cent[20]. The same effect was found by Shergold and Parkin[26] for the flotation of ilmenite with oleate. However, in both the apatite and ilmenite systems, an excessive conditioning time (>10 minutes) caused a reduction in the flotation response.

Other preliminary experiments in the fluorite-oleate system indicate that oxygen is consumed by the system. Research is in progress to confirm these initial findings, and a suggested explanation of these results requires further consideration and analysis of the hydrophobic character of the adsorbed calcium oleate species.

HYDROPHOBIC CHARACTER

The flotation response of semisoluble salt minerals is determined by the hydrophobic character of the surface—that is, the level of collector adsorption, the collector type, and, most importantly, the nature of adsorbed collector species. Frequently, measurements of the contact angle are used to quantify the hydrophobic character of surfaces[27,28]; but contact-angle measurements are equilibrium or pseudo-equilibrium measurements rather than a dynamic measure of the hydrophobicity[29], and, in this regard, the attachment times and contact angles at the surface of selected semisoluble salt minerals were determined with a high-speed video/contact-angle goniometer system. In many instances, the hydrophobic character, as assessed by both equilibrium and kinetic measurements, was significantly dependent on the temperature, oxygen partial pressure, and oleate concentration.

Temperature effect

As described earlier, one of the most intriguing and important phenomena in the flotation of fluorite and also of other semisoluble salt minerals is the observed temperature dependence. In this regard, the hydrophobicity of the selected semisoluble salt minerals was measured as a function of the solution temperature.

The measured equilibrium contact angles are presented in Figure 9 as a function of the temperature. The contact angle at the surface of fluorite (pH = 8,1, 10^{-5} M oleate) at room temperature was found to be 68 to 70°, and the attachment time was 260 to 270 ms. However, no attachment was possible on apatite and barite at 10^{-5} M oleate. At 10^{-4} M (pH = 8,2), barite and apatite exhibited equilibrium contact angles of 60° and 40°, respectively, and the attachment time was estimated to be of the order of 500 ms. Increasing the solution temperature to above 60 °C resulted in an increase in the contact angle to between 90 and 95° for fluorite and to 80° for apatite and barite. Furthermore, and most importantly, the corresponding attachment time for fluorite was found to decrease by

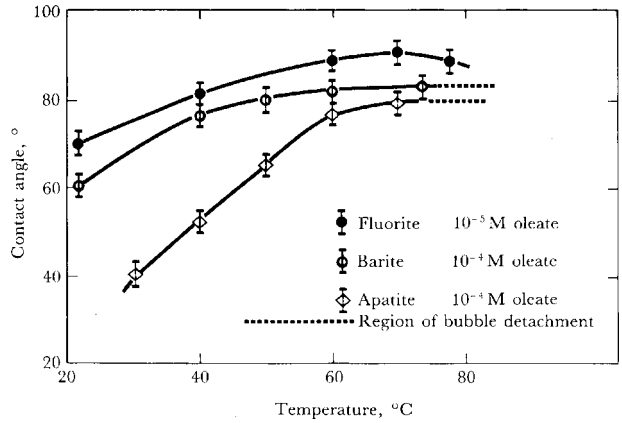
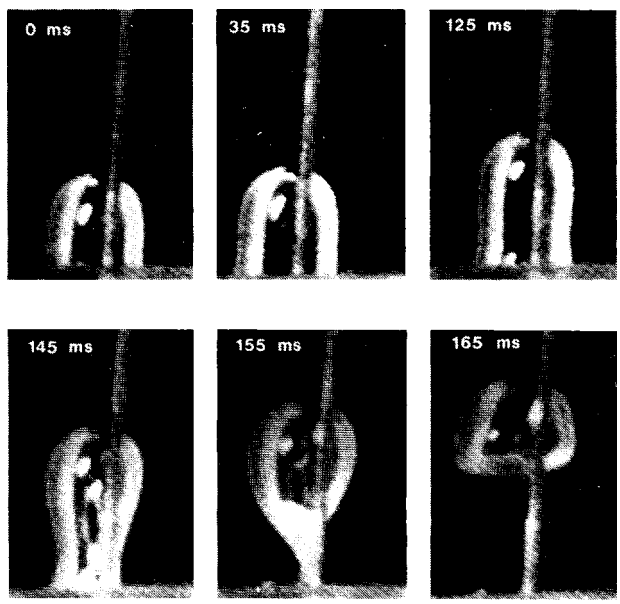


Figure 9. Contact-angle measurements on fluorite, barite, and apatite surfaces as a function of temperature; bubble size = 4,0 mm

almost one order of magnitude, to between 20 and 22 ms. This significant change in the hydrophobicity was reflected also in the flotation response of fluorite and apatite (see Figures 6 and 7). The higher temperatures might cause some interaction or structural change of the adsorbed oleyl radicals to enhance the hydrophobicity of the system. These observations are for freshly prepared surfaces; evidence has been reported that aged surfaces do not exhibit the same behaviour[12].

In addition to these findings, it was observed that the air-bubble attachment results in the accumulation of what appears to be calcium oleate soap in a small pile at the air-fluorite interface. This phenomenon may account for the air avidness (dry froth) reported by Cook and Last[22].



Fluorite on oleate 10^{-4} M, 77 °C

Figure 10. Time-sequence photographs for the attachment on an air bubble at the fluorite surface; bubble size = 4,0 mm

Although bubble attachment was found to be rapid, it was observed that bubble detachment occurs for temperatures exceeding 77 °C (Figure 10). Photographs of the time sequence for detachment from fluorite at 10^{-4} M oleate and 77 °C are presented in Figure 10. Such instabilities of the attached bubble have been observed for the quartz-amine system and have been related to the observed dynamic surface-tension effect for equilibration of the air-water interface[30]. In the fluorite-oleate and apatite-oleate system, it seems that other factors must be considered. For example, time-sequence photographs indicate that the contact angle does not change significantly with time, and, under certain circumstances, a film residue can be seen at the bubble surface upon detachment. These observations suggest that detachment occurs because of the buoyant force exceeding the forces that hold the multilayers of calcium oleate soap at the fluorite surface.

Oxygen effect

Similarly to the temperature effect, oxygen can enhance the hydrophobicity of the fluorite-oleate system. The effect of oxygen on measurements of the bubble-attachment time is shown in Table 1. Also, the increase in hydrophobicity is reflected in the flotation response of fluorite (Figure 8).

TABLE 1

The effect of oxygen on measurements of bubble attachment at a fluorite surface

Conditioning time = 20 min
Oleate concentration = 10^{-5} M
pH = 8,1
Bubble size = 3,8 mm

Gas phase	Contact angle °	Attachment time ms
Air (22 °C)	70-73	260-270
Oxygen (22 °C)	90-92	20-25

It is interesting to note that, at higher temperatures as well as at increased oxygen potential, the attachment time decreases by about one order of magnitude. These results suggest that temperature as well as oxygen may be important in the interaction or structural modification of the adsorbed oleate species. Shergold and Parkin[26] cited the work of Dorakhina[31] and Markley[32] and suggested that unsaturated oleic acid is oxidized slowly by atmospheric oxygen to hydroperoxide, then to oxirane, and is finally adsorbed at the mineral-water interface as epoxy films. This aspect is discussed in more detail in the section on double-bond reactivity.

Concentration effect

The effect of oleate concentration at the surface of fluorite was examined by measurements of the equilibrium contact angle and bubble-attachment

time. The results are presented in Table 2. Although the concentration of oleate has a significant effect on the hydrophobicity, an excessive addition of oleate results in the detachment of the air bubble together with a residue of the surface calcium oleate film in about 230 ms. Again, such instability of bubble attachment may also be related to the forces holding the multilayer calcium oleate soap at the surface. These observations may help to explain the poor flotation response that has been observed for calcite at high concentrations of long-chain fatty-acid collectors[33].

TABLE 2

The effect of oleate concentration on measurements of bubble attachment at a fluorite surface

Temperature = 22 °C
Gas phase = air
Conditioning time = 10 min
pH = 8,1
Bubble size = 3,8 mm

Oleate concentration M	Contact angle °	Attachment time ms
1×10^{-6}	No contact	-
5×10^{-6}	54-56	1000-1500
1×10^{-5}	68-70	260-279
1×10^{-4}	85-87	40-50
1×10^{-3} (pH 10,0)	90-92	20-22*

* Bubble detachment occurs after 230 ms

Recent contact-angle measurements in our laboratory indicate that the adsorption phenomena at the air-water interface have a significant effect on the hydrophobic character of semisoluble minerals with adsorbed oleate. The results are given in Table 3. For example, in the case of calcite, bubble attachment is difficult for an oleate concentration of 10^{-4} M at a pH value of 10,0. However, if the calcite sample is removed from the oleate solution, gently shaken to remove gravitational water, and replaced in fresh water at the same pH, bubble attachment is facilitated and a contact angle of 53 to 55° is realized. A similar phenomenon was observed for apatite.

TABLE 3

Measurements of bubble attachment (air, 22 °C) for selected semisoluble salt minerals in 10^{-4} M oleate solution and in water at a pH value of 10,0

Mineral	Contact angle, °	
	Oleate solution (γ_{AW} = 53,1 dyn/cm)	Fresh water (γ_{AW} = 71,7 dyn/cm)
Calcite	No contact	53-55
Apatite	No contact	50-55

These results provide further insight into flotation practice. High concentrations of oleate may be required to achieve the desired level of collector adsorption at the mineral interface; however, the bubble-attachment process under the same circumstances may be inhibited. These observations might explain some situations in which oleate adsorption is accomplished at high pulp density and then the pulp is diluted with fresh water for the flotation step. Such is frequently the procedure for the flotation of phosphate rock.

Double-bond reactivity

Scattered throughout the technical literature on oleate flotation are suggestions that the double-bond reactivity of oleate accounts for its effectiveness as a collector in non-sulphide flotation systems. Some evidence suggests that cross-linking may occur between oleate chains via an epoxide linkage leading to a polymerized layer of collector molecules with greater hydrophobic character[26,31,32,34]. Even 30 years ago, the possibility of such phenomena was recognized from an infrared study of the fluorite-oleate system[14]:

> 'Of particular interest is the diminishing of the *trans-* and *cis-* C = C bonds. This may possibly be explained by lateral polymerization following chemisorption. This characteristic of oleic acid may explain its outstanding properties as a collector compared with other long-chain fatty acids.'

Notwithstanding these evidences, it seems that the significance of double-bond interaction has not been given sufficient consideration in the study of non-sulphide flotation systems, fluorite in particular. One reason for the lack of attention may be the difficulty in detecting double-bond oxidation and cross-linking of chains.

Recently, Brando[34] conducted an extensive study on the magnesite-oleate system using multiple specular-reflection-absorption spectrometry. It was observed that the reactivity of the C = C double bond of the oleyl radical was responsible for the increased collecting power. Apparently, the hydroperoxide formed in the solution (because of auto-oxidation) converted to epoxide at the mineral surface. Subsequent reaction occurs because of the polymerization of epoxide to form a polyether structure. This epoxide-polyether film is strongly attached to the mineral surface and difficult to remove; but the polar carboxylate groups of the oleate are unaffected by the oxidation-polymerization of the hydrocarbon chain. The sequence of the reaction probably proceeds by the following mechanism[31,32,34]:

Formation of hydroperoxide

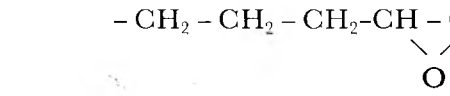
The initial step of oxidation of unsaturated fatty acid is not the rupture of the double bond but the reaction with one of the hydrogens of the neighbouring methylene group to form isomers of monohydroperoxide:

$$-CH_2-CH_2-\underset{\displaystyle O-OH}{\underset{|}{CH}}-CH=CH-CH_2-CH_2-$$

Formation of epoxide

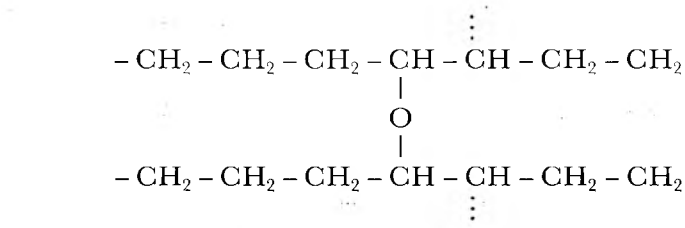
Hydroperoxides are generally reactive compounds. The double bond may rupture with the for-

mation of secondary compounds such as epoxides with the oxirane ring positioned at the place of the former double bond of the unsaturated alkyl group:



Polymerization of adsorbed epoxide

Polymerization of the adsorbed epoxide at the surface may take place by the reaction of the oxygen from an oxirane ring of a hydrocarbon chain with a neighbouring chain, thus forming a polymerized surface complex.



Any one of these adsorbed surface species may be responsible for the observed increase in hydrophobicity of these systems. The identification and stabilization of such a species would add a new dimension to flotation chemistry.

CONCLUDING REMARKS

During a consideration of data in the literature and data from our ongoing research programme, it became evident that the nature of a double-bond interaction of adsorbed oleate species is not well established. Such interaction will depend on the properties of the surface, loading of oleate on the surface, composition of the aqueous phase, temperature, and oxygen potential. If the conditions for reactions involving surface oxidation and polymerization between unsaturated collector salts can be established, the implications are far-reaching. Catalysts could be developed to promote such interactions, perhaps even for apatite, barite, scheelite, or metallic minerals. In this regard, efforts to describe these systems more accurately with respect to temperature and oxygen potential are in progress.

To advance our understanding in this area, it is mandatory that *in situ* spectroscopy research should be initiated for the study of flotation chemistry. During the past decades, some have doubted the significance of *ex situ* spectroscopy for the analysis of adsorption reactions encountered in flotation systems. Advances made for *in situ* measurements are reported in the chemistry literature[35,36], and researchers in flotation chemistry must turn their attention to applying these techniques to the study of flotation systems. Efforts are being made at the University of Utah to make such measurements.

Finally, the impact of flotation chemistry on the hydrophobic character of a surface should be established by kinetic as well as equilibrium measurements. Measurements of bubble-attachment time and attached-bubble stabilities are much more significant indicators of hydrophobicity in the context of flotation separations. Such measurements should be incorporated into our studies of flotation chemistry.

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